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Ion chromatography determination of anionic change in surface and ground water due to industrial effluents in Jammu (J&K), India

Sajaad Iqbal Khan, Raj Kumar Rampal* and Nishu

Department of Environmental Sciences, University of Jammu, Jammu (J&K), INDIA
*Corresponding author. E-mail: rajkrampal@gmail.com

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Abstract: In present investigation of anionic (fluoride, chloride, bromide, phosphate and sulphate) change in surface and ground water due to industrial effluents by ion chromatography technique has been determined in area of Jammu using Ion-chromatograph (IC-850).Surface and ground water samples were taken before and after discharge of industrial effluents. All required standards for calibration and all the samples (water as well as industrial effluents) have been prepared by using ultra pure water obtained from M Millipore. Both the peak height (PH) and peak area (PA) were used to assess the IC signals. All the peaks for anions were clear with good resolution and there were no interactions between them. The total time for anion analysis was recorded to be about 28 minutes .Anions like fluoride exhibited drastic change in concentration in surface and ground water samples taken after discharge of industrial effluents.

Keywords: Common anions, Ground water, Industrial effluents, Ion chromatography and Surface water

INTRODUCTION

The quality of drinking-water is a powerful environmental determinant of health. Drinking-water quality management has been a key pillar of primary prevention for over one-and a half centuries and it continues to be the foundation for the prevention and control of waterborne diseases. Water is essential for life, but it transmits diseases in countries in all continents – from the poorest to the wealthiest. The most predominant waterborne disease, diarrhoea, has an estimated annual incidence of 4.6 billion episodes and causes 2.2 million deaths every year (WHO, 2010) Fluorine is a common element that does not occur in the elemental state in nature because of its high reactivity. It accounts for about 0.3 g/kg of the Earth's crust and exists in the form of fluorides in a number of minerals, of which fluorspar, cryolite and fluorapatite are the most common. The oxidation state of the fluoride ion is -1.Fluoride may be an essential element for animals and humans. For humans, however, the essentiality has not been demonstrated unequivocally, and no data indicating the minimum nutritional requirement are available. To produce signs of acute fluoride intoxication, minimum oral doses of at least 1 mg of fluoride per kg of body weight were required (Janssen *et al.,* 1988). Chlorides are widely distributed in nature as salts of sodium (NaCl), potassium (KCl), and calcium ($CaCl_2$). A normal adult human body contains approximately 81.7 g chloride. On the basis of a total obligatory loss of chloride of approximately 530 mg/day, a dietary intake for adults of 9 mg of chloride per kg of body weight has been recommended (equivalent to slightly more than 1g of table salt per person per day). For children up to 18 years of age, a daily dietary intake of 45 mg of chloride should be sufficient. A dose of 1 g of sodium chloride per kg of bodyweight was reported to have been lethal in a 9-week-old child. Bromide (Br^-) is the anion of the element bromine, which is a member of the common halogen element series that includes fluorine, chlorine, bromine and iodine. The atomic weight of bromine is 79.909. Bromine is a dense mobile dark liquid at room temperature that freezes at -7 °C and boils at 58°C (Cotton and Wilkinson, 1962). A phosphate, an inorganic chemical, is a salt of phosphoric acid. Organic phosphates are important in biochemistry, biogeochemistry and ecology. Inorganic phosphates are mined to obtain phosphorus for use in agriculture and industry. At elevated temperatures in the solid state, phosphates can condense to form pyrophosphates. Sulphate occur naturally in numerous minerals, including barite ($BaSO_4$), epsomite ($MgSO_4.7H_2O$) and gypsum ($CaSO_4.2H_2O$) (Greenwood and Earnshaw, 1984). Atmospheric sulphur dioxide, formed by the combustion of fossil fuels and in metallurgical roasting processes, may contribute to the sulphate content of surface waters. Sulphur trioxide, produced by the photolytic or catalytic oxidation of sulphur dioxide, combines with water vapour to form dilute sulphuric acid, which falls as "acid rain" (Delisle and Schmidt, 1977).

Rapid industrialization has led to a severe deterioration in water quality in the country's lakes, rivers and ground

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water. With increase in industrialization various forms of hazardous chemical are directly discharged in to the water bodies that pollute all type of water including ground water which is the main source of drinking water supply throughout the world thereby causing various serious health problems on the globe. Industries are associated with effluent characterized by biological oxygen demand and suspended solids, and the effluent is high in all anions concentration (Ijeoma and Achi, 2011). In present studies determination of anionic (fluoride, chloride, bromide, phosphate and sulphate) change in surface and ground water due to industrial effluents by ion chromatography technique has been done in area of Jammu using Ion-chromatograph (IC-850).

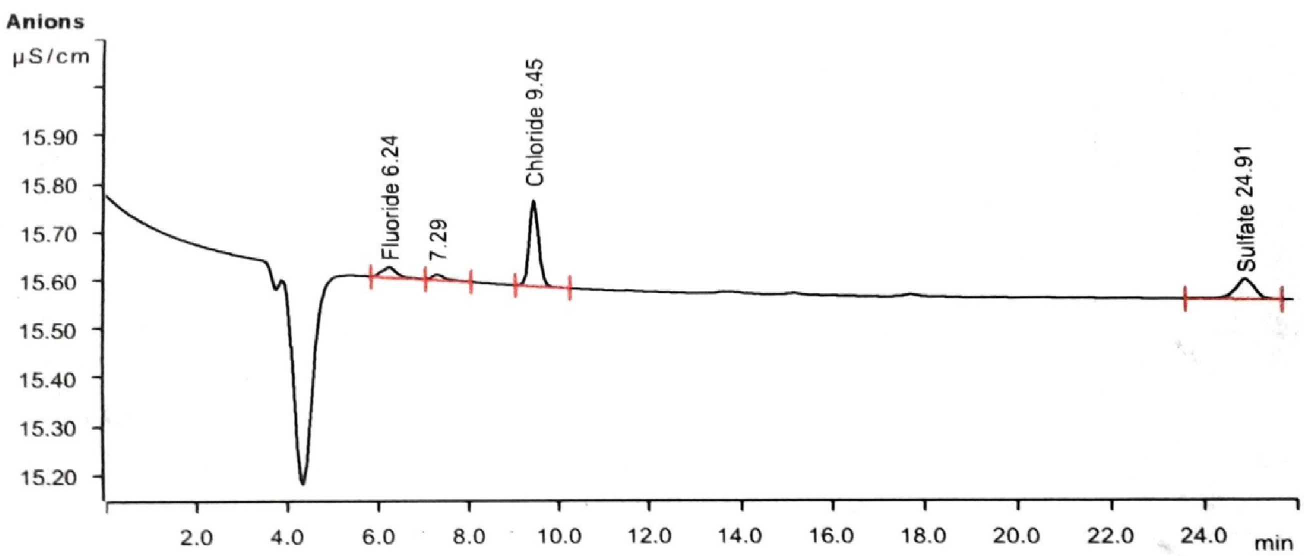
MATERIALS AND METHODS

Jammu is located 74^0 24' and 75^0 18', East longitude and 32^0 50' and 33^{0}30' North latitude. Jammu district has a sub tropical climate with hot and dry climate in summer and cold climate in winter. Water samples were collected from three locations before discharge of industrial effluents in Jammu, (i.e. Sample I-III): three locations after discharge of industrial effluents in Jammu (i.e.Sample VIII-X) and four samples of industrial effluents (i.e. Sample IV –VII) from Gangyal SIDCO industrial area of Jammu (Table 1). The determination of anionic (fluoride, chloride, bromide, phosphate and sulphate) in all samples (Sample TWI to TWX) were carried out using 850 professional IC system supplied from Metrohm, Switzerland. The system was connected to a PC-controller; Rapid start – click and analog output for connection to external data systems with or without chemical suppression. For automation tasks, the system was fully automatic, the 250/4.0 I C column for separation of mixture solution and the 863 Compact IC Auto sampler was used for injecting 20µm sample into IC for analysis. The Metrohm 850 Compact IC system was characterized by Built-in 6-way injection valve, Low-pulsation double piston pump with flow range of 0.2 to 10 ml/min and maximum pressure of 35 MPa (350 bar,),Pulsation dampener, Insulated column compartment, Detector temperature stabilized to better than 0.01°C with temperature range of 25-45°C in 5°C steps, Data source conductivity detector, Integration automatic, Eluent composition 3.2mM Na_2CO_3+1mM $NaHCO_3$, flow rate was constant 0.700 ml/min.

RESULTS AND DISCUSSION

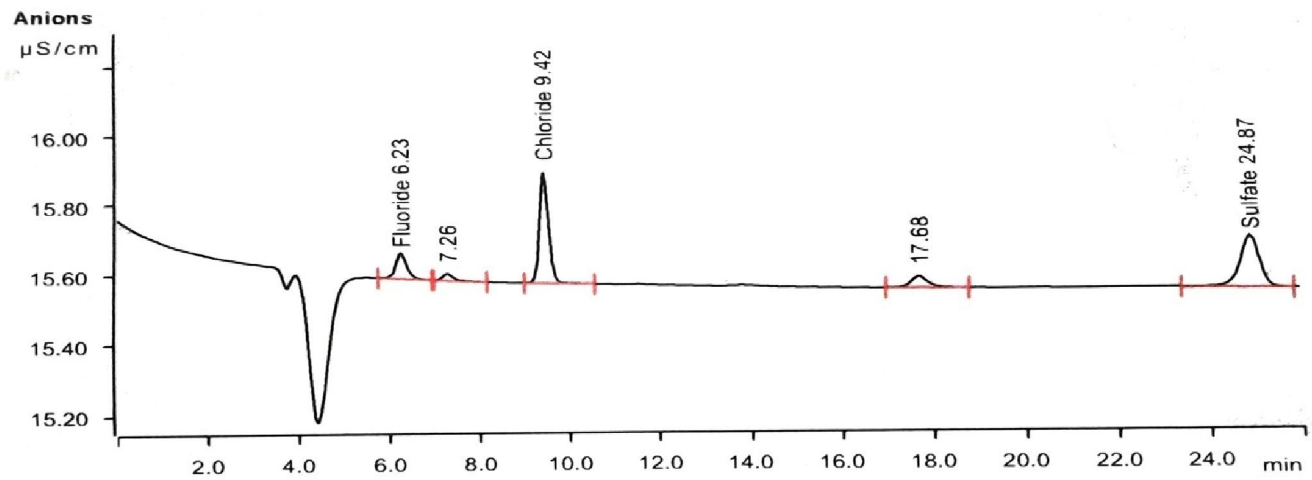
Figs. 1-10 and Table 2 illustrated the results of anion determine by IC technique in various samples at different locations as shown in Table 1.

All the sampling sites showed variation in concentration of fluoride. The highest concentration of fluoride was recorded at 'TW X' and lowest concentration was recorded at 'TW I' which is only sampling site shows the fluoride concentration within permissible limit but above desirable limit, according to IS 10500:1991 standards for



Peak number	Retention time min	Area (µS/cm) x min	Height µS/cm	Concentration ppm	Component name
1	6.242	0.0086	0.022	1.147	Fluoride
2	7.290	0.0040	0.011	invalid	
3	9.447	0.0430	0.176	8.938	Chloride
4	24.907	0.0206	0.041	6.091	Sulfate

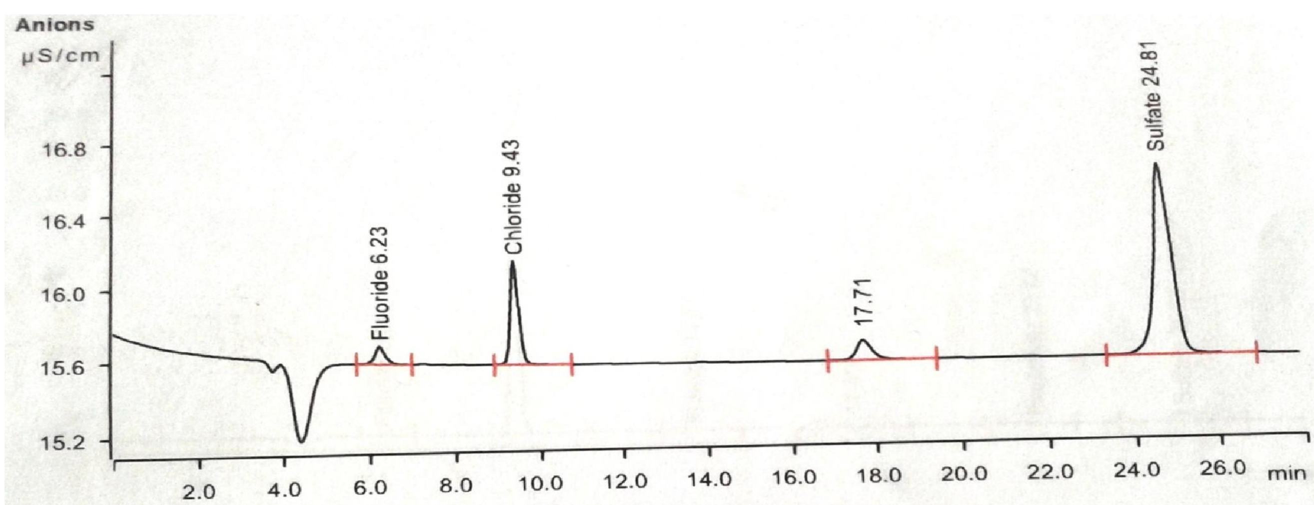
Fig. 1.*Chromatogram of common anions in drinking water sample for Jammu University.*



Peak number	Retention time min	Area (µS/cm) x min	Height µS/cm	Concentration ppm	Component name
1	6.232	0.0216	0.075	2.881	Fluoride
2	7.255	0.0059	0.021	invalid	
3	9.422	0.0749	0.319	15.574	Chloride
4	17.680	0.0144	0.033	invalid	
5	24.873	0.0737	0.148	21.825	Sulfate

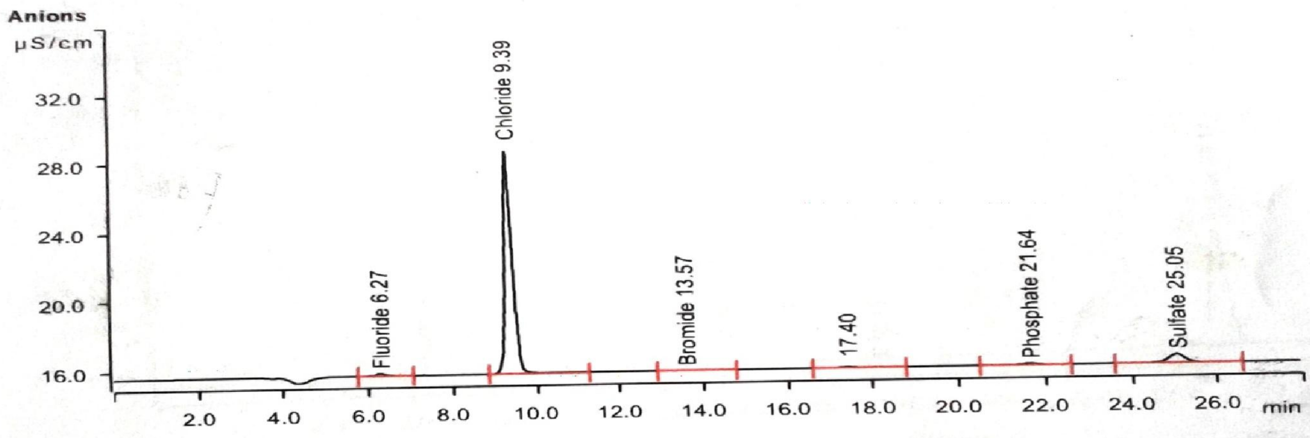
Fig. 2. *Chromatogram of common anions in river water before industrial discharge sample for Tawi Jammu.*

drinking water and Industrial discharge . More over its has been observed from present study that the sampling sites (TW I, TW II, and TW III) before discharge of industrial effluent show less concentration of fluoride than that of the sampling sites (TW VIII, TW IX and TW X) after discharge of industrial effluents. Khattak (2011) has also reported that industrial effluents were responsible for changing fluoride concentration. Many epidemiological studies of possible adverse effects of the long-term ingestion of fluoride in drinking-water have clearly established that fluoride primarily produced effects on skeletal tissues (bones and teeth). Low concentrations



Peak number	Retention time min	Area (µS/cm) x min	Height µS/cm	Concentration ppm	Component name
1	6.227	0.0293	0.100	3.914	Fluoride
2	9.432	0.1344	0.573	27.958	Chloride
3	17.712	0.0495	0.112	invalid	
4	24.813	0.5144	1.040	152.221	Sulfate

Fig. 3.*Chromatogram of common anions in hand pump water sample for Sidhra Jammu.*

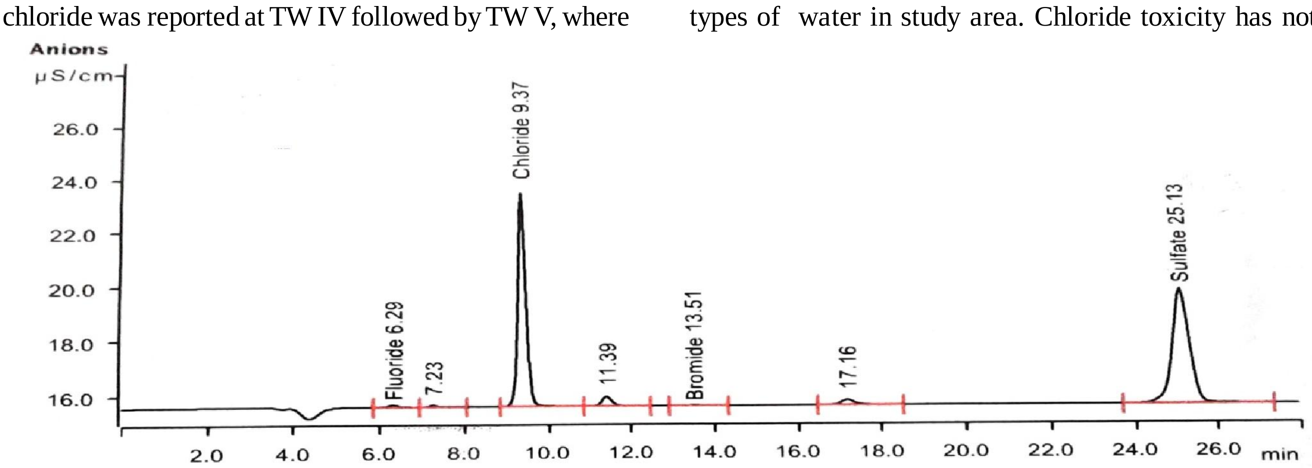


Peak number	Retention time min	Area (µS/cm) x min	Height µS/cm	Concentration ppm	Component name
1	6.267	0.0459	0.155	11.545	Fluoride
2	9.388	2.8881	12.955	1075.463	Chloride
3	13.573	0.0119	0.017	10.681	Bromide
4	17.398	0.0277	0.065	invalid	
5	21.643	0.0443	0.097	57.587	Phosphate
6	25.045	0.2521	0.510	126.875	Sulfate

Fig. 4.*Chromatogram of common anions in Pepsi industrial effluent water sample for SIDCO-1.*

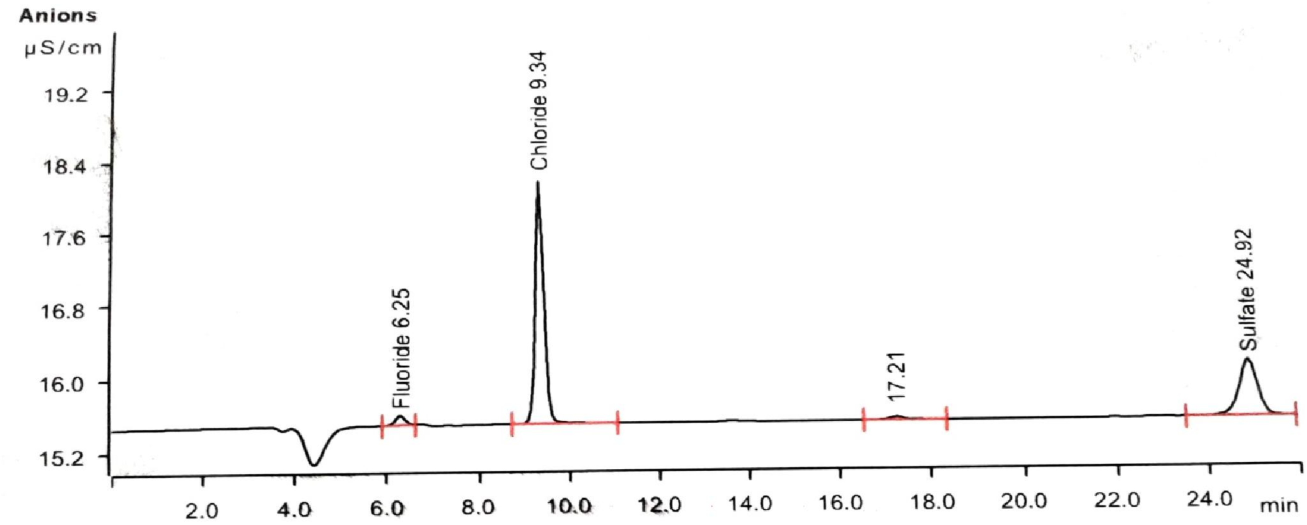
provide protection against dental caries, especially in children.

Concentration of chloride in all the sampling sites before and after discharge of industrial effluents was observed to be within permissible limits of 250 mg/l according to IS 10500:1991. There was variation in concentration of chloride in all sampling sites. The high concentration of chloride was reported at TW IV followed by TW V, where as lowest concentration was reported at TW I followed by TW II. On comparative basis the concentration of chloride was observed to be higher in sampling sites (TW VIII, TW IX and TW X) after the discharge of industrial effluent than that of sampling sites (TWI, TWII, and TW III) before discharge of industrial effluent thereby exhibiting impact of industrial effluent in all types of water in study area. Chloride toxicity has not



Peak number	Retention time min	Area (µS/cm) x min	Height µS/cm	Concentration ppm	Component name
1	6.287	0.0290	0.094	7.291	Fluoride
2	7.233	0.0171	0.079	invalid	
3	9.367	1.8101	7.995	674.050	Chloride
4	11.388	0.1072	0.378	invalid	
5	13.512	0.0075	0.012	6.715	Bromide
6	17.158	0.0839	0.208	invalid	
7	25.128	2.0533	4.266	1033.226	Sulfate

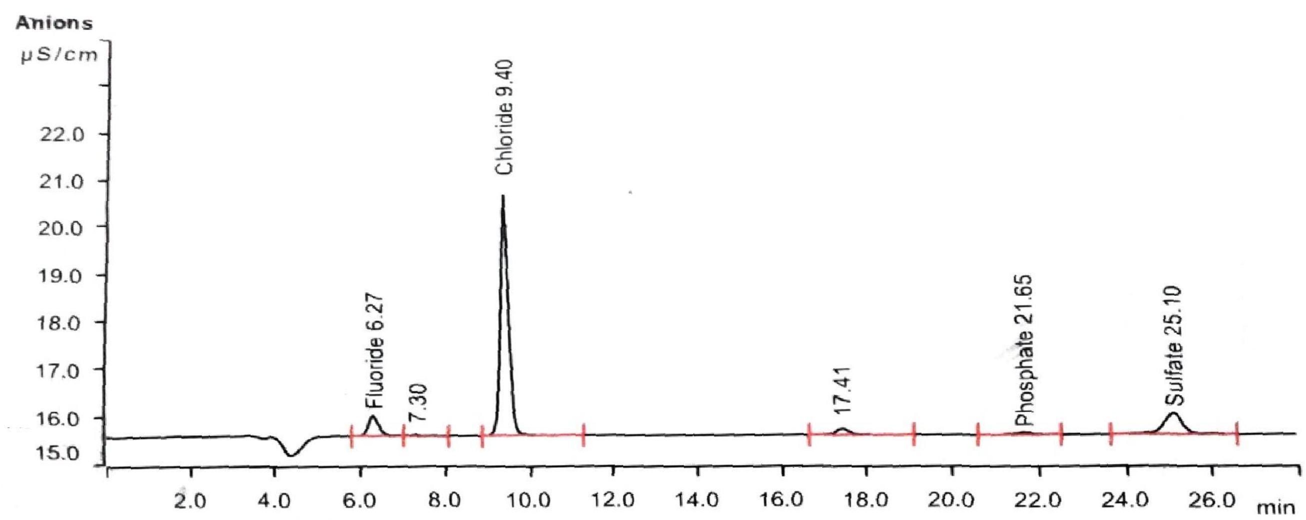
Fig. 5.*Chromatogram of common anions in Ink industrial effluent water sample for SIDCO-2.*



Peak number	Retention time min	Area (µS/cm) x min	Height µS/cm	Concentration ppm	Component name
1	6.252	0.0282	0.111	3.736	Fluoride
2	9.340	0.6042	2.693	122.841	Chloride
3	17.212	0.0161	0.039	invalid	
4	24.918	0.2975	0.622	87.969	Sulfate

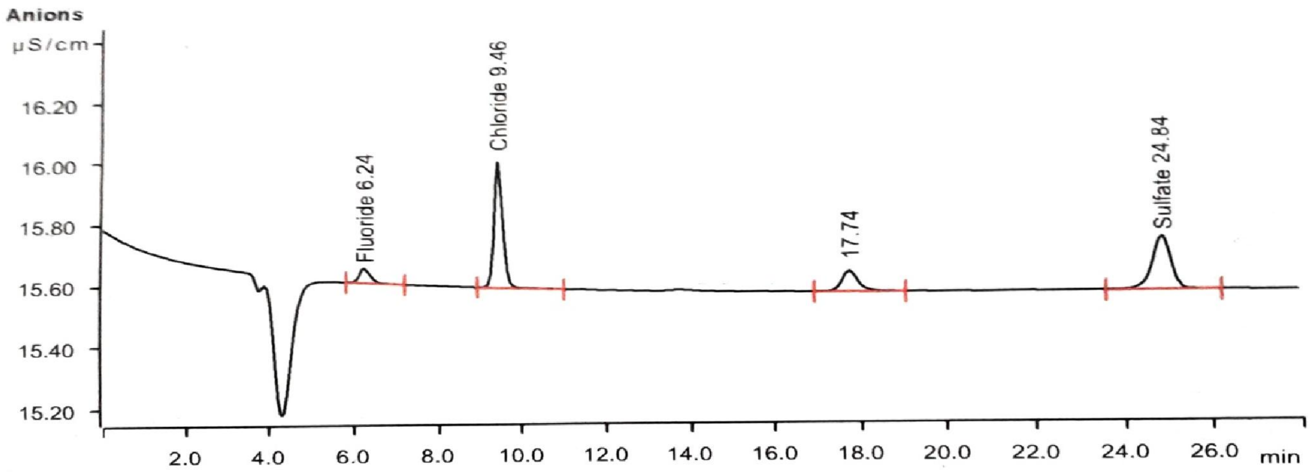
Fig. 6. *Chromatogram of common anions in Detergent industrial effluent water sample for SIDCO-3.*

been observed in humans except in the special case of impaired sodium chloride metabolism, e.g. in congestive heart failure. Healthy individuals can tolerate the intake of large quantities of chloride provided that there is a



Peak number	Retention time min	Area (µS/cm) x min	Height µS/cm	Concentration ppm	Component name
1	6.273	0.1249	0.442	8.277	Fluoride
2	7.295	0.0070	0.028	invalid	
3	9.400	1.1585	5.065	117.775	Chloride
4	17.407	0.0567	0.135	invalid	
5	21.652	0.0185	0.040	7.143	Phosphate
6	25.095	0.2193	0.443	32.421	Sulfate

Fig. 7. *Chromatogram of common anions in mix- industrial effluent water sample for SIDCO-4.*

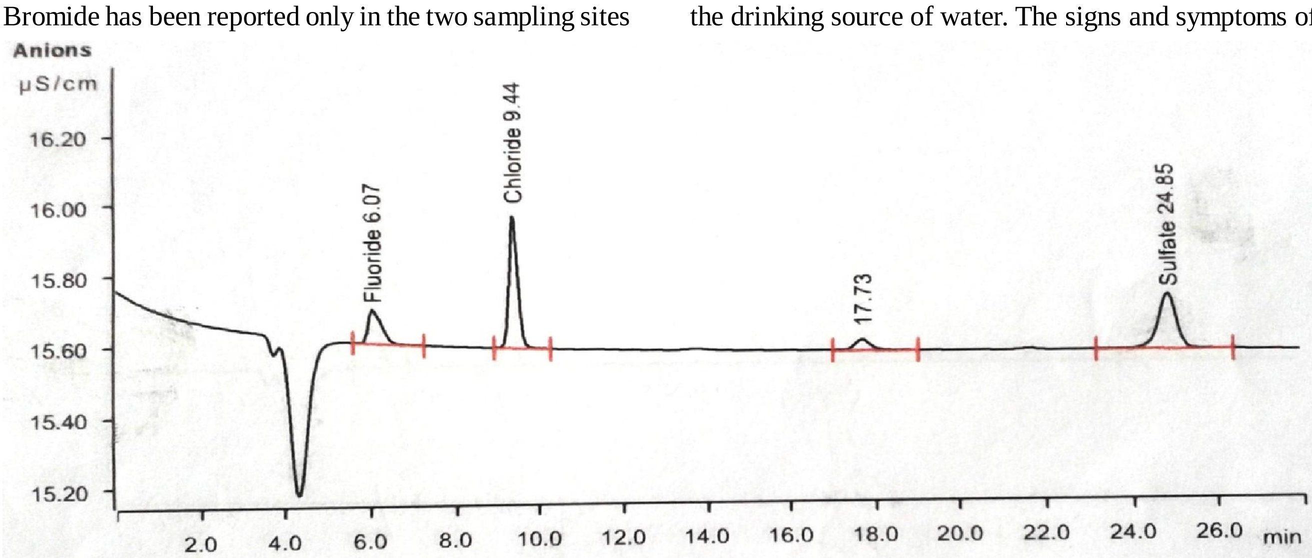


Peak number	Retention time min	Area (μS/cm) x min	Height μS/cm	Concentration ppm	Component name
1	6.242	0.0155	0.049	2.074	Fluoride
2	9.457	0.1006	0.407	20.928	Chloride
3	17.742	0.0298	0.066	invalid	
4	24.843	0.0836	0.168	24.748	Sulfate

Fig. 8.*Chromatogram of common anions in drinking water sample for SIDCO industrial area Jammu.*

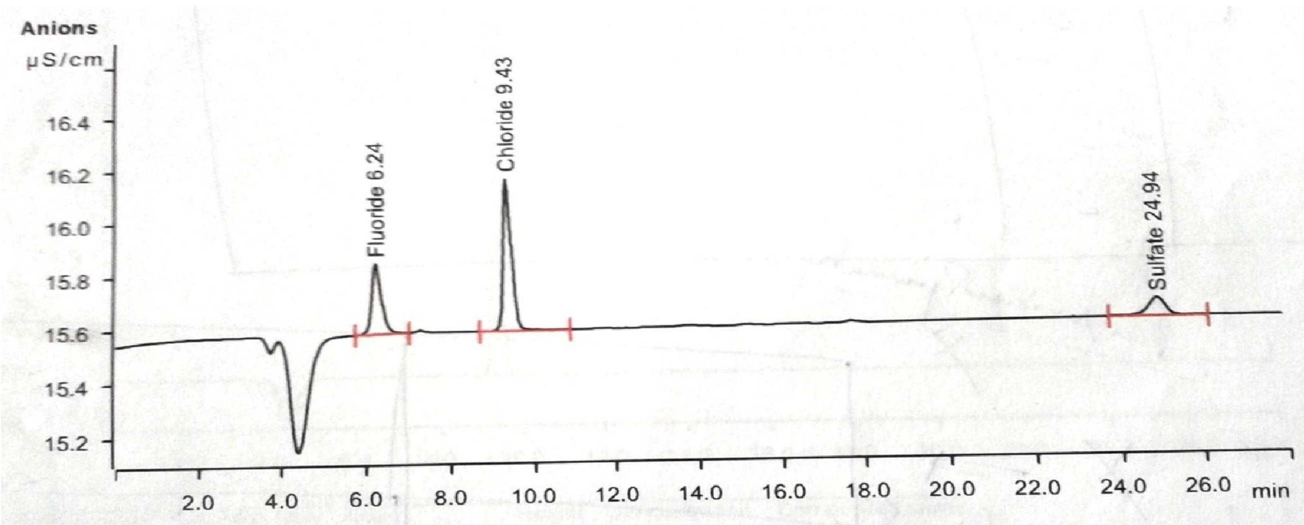
concomitant intake of fresh water. Little is known about the effect of prolonged intake of large amounts of chloride in the diet. As in experimental animals, hypertension associated with sodium chloride intake appears to be related to the sodium rather than the chloride ion (WHO, 2010).

Bromide has been reported only in the two sampling sites TW IV and TW V of industrial area which clearly indicated the bromide pollution in waters of industrial area. There is no such standard for bromide concentration in industrial effluent but according to WHO the concentration of bromide in fresh water is only 0.5mg/l that clearly shows industrial discharge ultimately pollute the drinking source of water. The signs and symptoms of



Peak number	Retention time min	Area (μS/cm) x min	Height μS/cm	Concentration ppm	Component name
1	6.065	0.0363	0.098	4.847	Fluoride
2	9.443	0.0900	0.373	18.726	Chloride
3	17.727	0.0140	0.031	invalid	
4	24.850	0.0781	0.154	23.120	Sulfate

Fig. 9.*Chromatogram of common anions in river water sample for Tawi after industrial discharge Jammu.*



Peak number	Retention time min	Area (µS/cm) x min	Height µS/cm	Concentration ppm	Component name
1	6.243	0.0743	0.268	18.686	Fluoride
2	9.433	0.1333	0.571	49.650	Chloride
3	24.943	0.0334	0.068	16.829	Sulfate

Fig. 10. *Chromatogram of common anions in hand pump water sample for industrial area Jammu.*

Table 1. Water and industrial effluents samples from various locations in Jammu (J&K).

Sample	Location	Type of water
Sample TWI	Tap water University of Jammu.	Drinking water
Sample TW II	The river Tawi water before discharge of industrial effluent.	River water
Sample TW III	Sidhra Jammu.	Hand-Pump
Sample TW IV	SIDCO Industrial area-1	Pepsi industry effluent
Sample TW V	SIDCO Industrial area-2	Ink-industry effluent
Sample TW VI	SIDCO Industrial area-3	Detergent industry effluent
Sample TW VII	SIDCO Industrial area-4	Mix industrial effluent
SampleTW VIII	Tap water SIDCO Industrial area	Drinking water
Sample TW IX	The river Tawi water after discharge of Industrial effluent	River water
Sample TW X	SIDCO Industrial area	Hand-pump

Table 2. Concentration of anions determined by IC in various samples at different locations of Jammu (J&K).

Sample	Type of anion (ppm)				
	Fluoride	Chloride	Bromide	Phosphate	Sulphate
Sample TWI	1.14< (1.5)	8.93<(250)	0	0	6.09<(200)
Sample TW II	2.88 >(1.5)	15.57<(250)	0	0	21.82<(200)
Sample TW III	3.91>(1.5)	27.45<(250)	0	0	152.22<(200)
Sample TW IV	11.54>(1.5)	1075.46>(1000)	10.68>(0.5)	57.58>(0.1)	126.87<(400)
Sample TW V	7.29>(1.5)	674.05<(1000)	6.75>(0.5)	0	1033.22>(400)
Sample TW VI	3.73>(1.5)	122.84<(1000)	0	0	87.96<(400)
Sample TW VII	8.27>(1.5)	117.77<(1000)	0	0	32.42<(400)
SampleTW VIII	2.07>(1.5)	20.92<(250)	0	0	24.74<(200)
Sample TW IX	4.84>(1.5)	18.72<(250)	0	0	23.12<(200)
Sample TW X	18.68>(1.5)	49.65<(250)	0	0	116.82<(200)

bromism relate to the nervous system, skin, glandular secretions and gastrointestinal tract (Leeuwen and Sangster, 1988).

Phosphate was reported only from one site TW IV of industrial area. Based on present investigation it shows that there was less Phosphate contamination in normal water type same has been reported by (Khattak, 2011). There is no specific standard for phosphate in industrial effluent but excess amount of phosphate is considered as pollution causing salt. Phosphate is a mineral that combines with calcium to form the hard structure of bones and teeth. High levels of phosphate can causes ever itchiness, lumps of calcium and phosphate in the bones, joints and blood vessels, causing brittle bones and painful joints bone disease.

Sulphate was detected in all sampling site, the highest concentration of sulphate was detected at TW V and lowest concentration was detected at TW I. On comparative basis the concentration of sulphate was observed to be higher in drinking and river water sampling sites (TWVIII, TWIX) after the discharge of industrial effluent than that of drinking and river water sampling sites (TWI, TWII) before discharge of industrial effluent thereby exhibiting impact of industrial effluent in drinking all types of water in study area. From the study it is concluded that all the concentration of sulphate were observed to be within permissible limit 200mg/l according to (BIS, 1991; ISO, 1992). But WHO has recommended no guideline for sulphate content in water. Higher concentration of sulphate in water sample from industrial area has been supported by observation made by Khattak (2011). Ingestion of 8 g of sodium sulphate and 7 g of magnesium sulphate caused catharsis in adult males (Cocchetto and Levy, 1981; Morris and Levy, 1983). Cathartic effects are commonly reported to be experienced by people consuming drinking-water containing sulphate in concentrations exceeding 600 mg/litre (DHEW, 1962; Chien, 1968).Dehydration has also been reported as a common side-effect following the ingestion of large amounts of magnesium or sodium sulphate (Fingl, 1980).

Conclusion

Overall analysis of the data revealed that concentration of fluoride, chloride, and sulphate exhibited higher values in sampling sites after discharge of industrial effluent then that of sampling sites before discharge of industrial effluent. There by exhibiting impact of industrial effluent in all types of water in study area. Whereas bromide and phosphate were observed to be absent in surface and ground water samples taken before as well as after discharge of industrial effluents**.**

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